

A NEW APPROACH FOR THE MANUFACTURE OF VEGETABLE TANNED LEATHER

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ABSTRACT

A study was made to assess, the quality of leathers produced by pre-treating the pelt with myrab followed by tanning with condensed tan materials as against the conventional practice of 'straight through' tannage and the comparative amount of tannins consumed for the same in each case. The results showed that in pieces pretreated with myrab, the subsequent penetration of condensed tan materials needed much less time than in those treated straightaway with condensed tan materials and their blends. Most of the properties of the leathers pretreated with myrab and followed by tanning in condensed tan materials were found to be better than those tanned directly with condensed tan materials and their blends.

This technique may therefore be advantageously followed for the manufacture of different types of vegetable tanned leathers with considerable economy in the use of condensed tannins.

In India, heavy leathers are generally made with the blends of myrab (*Terminalia Chebula*), babul (*Acacia Arabica*) and wattle (*Acacia Mollissima*) or only with wattle and myrab. The present trend of sole leather manufacture in India is to use more and more of myrab in the blend, since this tanning material is more easily available and its price is also comparatively low. These blends take about 2-3 months for the completion of heavy leather tannage. Considerable amount of sludge in the yard liquors is found to be deposited in course of tannage. Our studies showed¹ that the use of increased amount of myrab in the blend led to retarded penetration as was evident from non-uniform coloration of the cut section of the tanned piece. The slow penetration of the blend liquor might be due to the following reasons :

(a) When condensed tannins come in contact with acidic hydrolysable tannins, there is every possibility of the former getting polymerised, resulting in retarded penetration. This polymerisation of the condensed tan molecules depends on the relative amount of the hydrolysable tannins present in the blend.

(b) The myrab tans and nontans in the blend may undergo further hydrolysis forming bloom (sludge) in the tan liquor, and this may hinder the penetration of the blend liquor through the pelt.

(c) The myrab tan molecules being negatively charged² may have some affinity for the condensed tan molecules and when these are mixed together the resultant complex may have a slower rate of penetration.

Numerous references are available in the relevant literature in regard to heavy leather tannage using condensed tan materials like wattle and quebracho. However, very few seem to have worked with blends of hydrolysable and condensed tan materials. Presumably such blends did not lead to any significant advantage in quick tannage.

Benskin and Cheshire showed³ (as was also confirmed by our recent findings⁴) that the penetration of the tan liquor through the pelt was considerably increased when the pelt was brought to the isoelectric region.

Since increase in the proportion of myrab infusion in the blended tan liquor led to retarded penetration and more sludge formation, it was thought worthwhile to treat the pelt individually with these two types of tan materials in separate baths. This was expected to give us some idea about the efficiency of such a treatment vis-a-vis the conventional practice in respect of the quality of the leather produced and the amount of tannins consumed for the same.

Experimental

Penetration of tan liquors

(a) Myrab liquor :—Myrab liquor was prepared by two consecutive extractions of crushed myrab nuts with water in the ratio 1 : 4. The combined liquor was made upto pH 5 using sodium sulphite and the strength was then finally adjusted to 25°Bk.

b) Babul liquor :—Babul liquor was prepared in the usual way by extracting the crushed babul bark on the countercurrent principle. The liquor was also made upto 25°Bk.

(c) Mangrove liquor :—A liquor of 25°Bk was made from spray dried mangrove extract from Andaman mangrove bark (*Rhizophora mucronata*).

(d) Wattle liquor :—A solution of 25°Bk was made using commercial wattle extract (*Acacia mollissima*) of known strength.

(e) Blend of wattle and myrab :—Required volume of 25°Bk. Wattle liquor was mixed with known volume of 25°Bk myrab liquor (freshly leached) so as to make a blend of 2 : 1 respectively.

(f) **Blend of babul and myrab** :—Required volumes of babul and myrab leach liquors (25°Bk) were mixed in the ratio of 2 : 1 respectively.

Tanning procedure

A wet salted buffalo hide was soaked, limed and delimed in the usual way. The butt portion (5 mm thick) was then taken and cut into 8 pieces each measuring 15 cm × 10 cm. Four pieces were then put in myrab liquor and the pelt/liquor ratio was adjusted to 1 : 15. They were handled twice a day and examined each day for the extent of penetration. After 4 days when the myrab treated pieces were fully struck through, three of these pieces were washed and put separately in wattle, babul and mangrove liquors, keeping the pelt/liquor ratio at 1 : 15. The 4th piece was kept in the same myrab liquor for five more days.

In another series, 3 pieces of delimed pelt were put separately in wattle, babul and mangrove liquor keeping the pelt/liquor ratio same as before. After the completion of penetration the pieces were kept in the liquor for 5 more days.

In the first series i.e., with myrab pretreated pieces, wattle penetrated in 3 days whereas both babul and mangrove took 9 days to penetrate. All the pieces were kept in the respective liquors for 5 more days following complete penetration. In the second series wattle penetrated in 6 days, babul in 11 days and in the case of mangrove, penetration was not complete even after 40 days.

At the end of the stipulated period all the pieces were taken out and the adhering liquor was wiped off with moistened cotton wool. The pieces were kept in the dark for drying and then analysed for their chemical and physical properties. The residual liquors were also analysed for tan/nontan content. The results are given in the tables.

Discussion of results

From the results it was observed that in pieces pretreated with myrab the subsequent penetration of condensed tan materials needed much less time than in those treated straightway with condensed tan materials only. Mangrove liquor known for its poor diffusion capacity through the pelt⁵ penetrated through the myrab pretreated piece very quickly (9 days). In contrast, the original liquor failed to penetrate through the pelt even after 40 days. Likewise, wattle and babul liquors penetrated through the myrab pretreated pieces with comparative ease (in 3 and 9 days respectively) although such improvement was less marked than it was in mangrove. The penetration of the blended liquors took more time than the corresponding original condensed tan liquors.

The experiment thus showed that pretanning with myrab at pH 5 helped the penetration of condensed tan materials considerably. Presumably myrab containing more of phenolic nontans⁶ penetrate through the pelt with sufficient ease and this helps the opening up of fibres and fibrils. When the myrab pretreated pieces are put in condensed tan liquors containing tannins of varying particle size some of these tan particles easily pass through the already opened up fibrous network and get themselves lodged in the interstices of the fibres, displacing perhaps a part of myrab nontans already present there.

As regards degree of tannage, it was observed that the leather pretreated with myrab and followed by treatment with condensed tan materials indicated a higher degree of tannage than the one tanned without such pretreatment. The degree of tannage of the leather tanned with myrab was found to be the lowest with that of the leather tanned with the blends coming next. Exception was observed in the case of the leather tanned with original mangrove liquor, in which case even though penetration was not complete over a period of 40 days, the degree of tannage nevertheless was found to be higher than the one pretreated with myrab and subsequently treated with mangrove. This is presumably due to the fact that in course of the contact time of 40 days a good amount of mangrove tannins got highly polymerised and got themselves fixed up on the surface of the pelt thereby giving a higher degree of tannage.

When the pelts are pretreated with myrab infusion, the myrab tannins are probably for the most part fixed by nonionic protein groups, while the sorbed matter apparently is held chiefly by the cationic protein groups without cross-linking⁷. But when the myrab pretreated pieces are put in condensed tan molecules, most of the sorbed matter is likely to be replaced by the higher mol. wt. condensed tan aggregates giving rise to higher degree of tannage. In the case of the leathers tanned with blended liquors, the degree of tannage was found to be very low. Presumably, the blend prevented the quicker penetration of the tan molecules through the pelts and consequently yielded a low degree of tannage.

The final weight yield was higher in case of all the myrab pretreated pelts as compared to those treated with condensed tan materials alone. The pieces tanned with the blends showed low yield. The myrab pretreated piece tanned with wattle indicated about 6 percent more yield than the one tanned with wattle only. Similarly, myrab pretreated piece tanned with babul gave 10 percent more yield in comparison to that tanned with babul only. Myrab pretreated piece tanned with mangrove showed slightly more yield than the mangrove tanned piece, which was of course left in the mangrove liquor for quite a long time. The significant improvement in yield brought about by the myrab pretreatment might be due to the weight giving property of myrab. Since penetration and fixation were poor in the case of leathers tanned with the blends, the resultant yield was also poor.

The leathers pretreated with myrab followed by tannage with condensed tan materials showed almost the same Ts as those of the pieces tanned with the blends but a slightly lower value than those tanned with condensed tan materials only, myrab tanned piece as usual showing the lowest Ts. The higher Ts of the leather is generally ascribed to the strengthening of the existing cross-links and the formation of new cross-links between the polypeptide chains. According to Gustavson⁷ myrab tannin is probably for the most part fixed by the nonionic protein groups, while the sorbed matter is apparently held chiefly by the cationic protein groups without cross linking. When these myrab treated pieces were tanned with condensed tan materials, the sorbed portion of the extract is presumably replaced by the condensed tan materials, which are known to be powerful cross linking agents. Probably the condensed tan molecules themselves form new cross links and strengthen the existing cross-links of collagen, thereby raising the Ts of the leather.

The water absorption capacity of all the pieces pretreated with myrab showed least value followed by that of the leathers tanned with the blended liquors. The leathers tanned only with myrab, babul and wattle showed the highest and almost the same water absorption values after 24 hours. Mangrove tanned piece showed minimum water absorption. This is presumably due to the fact that mangrove tanned piece was tanned for 40 days and full penetration of the liquor through the pelt was not effected. Once dried, the mangrove tannin is known to be less soluble in water^{8,9}. The water absorption capacity of all the pieces was found to be more than what is usual for sole leather. This is expected since the pieces were neither heavily tanned nor oiled and rolled.

The abrasion resistance of all the pieces tanned with myrab followed by condensed tan materials showed the maximum value. The leathers tanned with the blend as well as those treated with myrab only came next. The leathers tanned with the condensed tan liquors showed the least resistance to abrasion. This may mean that even though myrab tan molecules are not efficient cross-linking agents, they do impart a good resistance to abrasion to the treated leather. In addition, myrab tannage, through its bloom formation inside the leather may also contribute to this increased resistance to abrasion.

The colour of all the pieces pretreated with myrab and followed by condensed tan liquor was the best of the series, that of the leathers tanned with the blends coming second. The leathers tanned with condensed tan liquors only, was the darkest in colour.

From the analysis of the spent tan liquors, it was observed that the liquors used for tanning the myrab pretreated pelts contained more of tans than those in which pelts were tanned without pretreatment. Wattle tan liquor used for tanning myrab pretreated pelt contained about 40 per cent more tannin in the

TABLE I
Analysis of the Tan Liquors

	Myrab	Wattle	Babul	Mangrove	Babul + Myrab (2 : 1)	Wattle + Myrab (2 : 1)
	Initial	Initial	Initial	Initial	Initial	Initial
	After tanning the deli- med pelts	After tanning the deli- med pelts	After tanning the deli- med pelts	After tanning the deli- med pelts	After tanning the deli- med pelts	After tanning the deli- med pelts
	67	69	57	67	55	68
Total solubles (gms./litre)	43	31	42	20	29	25
	Initial	Initial	Initial	Initial	Initial	Initial
	After tanning the deli- med pelts	After tanning the deli- med pelts	After tanning the deli- med pelts	After tanning the deli- med pelts	After tanning the deli- med pelts	After tanning the deli- med pelts
	34	47	30	34	37	41
Tans (gms./litre)	10	23	29	14	13	17.5
	Initial	Initial	Initial	Initial	Initial	Initial
	After tanning the deli- med pelts	After tanning the deli- med pelts	After tanning the deli- med pelts	After tanning the deli- med pelts	After tanning the deli- med pelts	After tanning the deli- med pelts
	33	22	27	33	18	27
Nontans (gms./litre)	33	8	13	6	16	7.5
	Initial	Initial	Initial	Initial	Initial	Initial
	After tanning the deli- med pelts	After tanning the deli- med pelts	After tanning the deli- med pelts	After tanning the deli- med pelts	After tanning the deli- med pelts	After tanning the deli- med pelts
	25	25	25	25	25	25
Strength of the liquor (°Bk)	20	12	15	14	15	12

TABLE II
Chemical and Physical properties of the Leathers (Chemical analysis on 14 per cent moisture basis)

Sl. No.	Leather tanned with	Insoluble ash (per cent)	Water solubles (per cent)	Hide substance (per cent)	Fixed tan (per cent)	Degree of tannage	Abrasion resistance (loss of thickness in mm for 500 revolutions)	Water absorption 2 hours	Ts 24 hours (°C)	Yield (per cent, oil defined pelt wt.)	Penetration (days)
1.	Myrab	Negligible	9.5	57.49	21.46	37.30	3.75	92.8	106.7	65	50
2.	Babul	do	10.12	51.14	26.74	52.30	4.45	106.5	112.8	82	55.35
3.	Wattle	do	13.59	46.69	27.70	59.30	4.69	92.5	100.3	85	62.15
4.	Mangrove	do	6.5	45.54	36.00	80.00	2.36	75.3	87.9	82	61.00
5.	Myrab followed by babul	do	10.77	48.87	28.30	58.70	2.79	78.3	84.4	80	65.27
6.	Myrab followed by wattle	do	14.42	44.50	29.01	65.40	2.92	71.1	76.2	82	68.65
7.	Myrab followed by mangrove	do	7.7	50.95	29.31	58.00	3.55	83.0	89.3	80	64.00
8.	Blend of myrab and babul	do	8.4	51.8	25.80	49.8	3.8	86.5	92.4	81	55.00
9.	Blend of myrab and wattle	do	9.4	50.6	26.0	51.4	4.0	75.2	82.3	83	60.0

4
11
6
10 per cent
remains even
after 40 days
9 After myra
3 tanning
9 (4 days)
15
8

spent liquor as compared to the corresponding residual liquor in respect of the pelts not subjected to any such pretreatment. Babul and mangrove liquors used for myrab pretreated pelts contained almost double the quantity of tannin in the spent liquors in each case as compared to the one for leathers tanned without any pretreatment. From the analytical figures of the spent liquors it is evident that the pelt used in condensed tan liquors alone had taken up about 60 percent of tannin from the wattle tan liquor whereas the myrab pretreated one absorbed only about 30 per cent. This showed that if the pelts are pretreated with myrab about 30 per cent less of wattle tannins are needed to achieve the desired properties in the resultant leather. The pelts tanned with babul and mangrove liquors as such absorbed about 77 per cent and 82 per cent of tannins respectively in contrast to the myrab pretreated pelts absorbing about 37 per cent and 62 per cent tannins i.e. about 40 per cent and 28 per cent less than the corresponding figures in the former series.

The experiment thus showed that if the delimed pelts are first treated with myrab around pH 5 for a few days till the penetration is completed and are then finally tanned in condensed tan liquors, a considerable saving of condensed tan extract may be effected. Penetration time of the condensed tan infusions through the myrab pretreated pelt is also considerably reduced, even though the overall tanning time with wattle and babul is slightly increased. In the case of mangrove however, the total tanning period is considerably reduced. Moreover, myrab pretreatment at the same time ensures most of the desirable properties in the final leather in respect of yield, degree of tannage, water absorption, abrasion resistance and colour as attained with other series in comparison. Since the myrab pretreatment is carried out around pH 5 the sludge formation in the liquor is also reduced to the minimum.

It therefore seems as though the same technique may be advantageously followed for the manufacture of sole leather (both pit and bag tanned), E.I. kips and skins, etc., with considerable resultant economy in the use of condensed tannins.

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